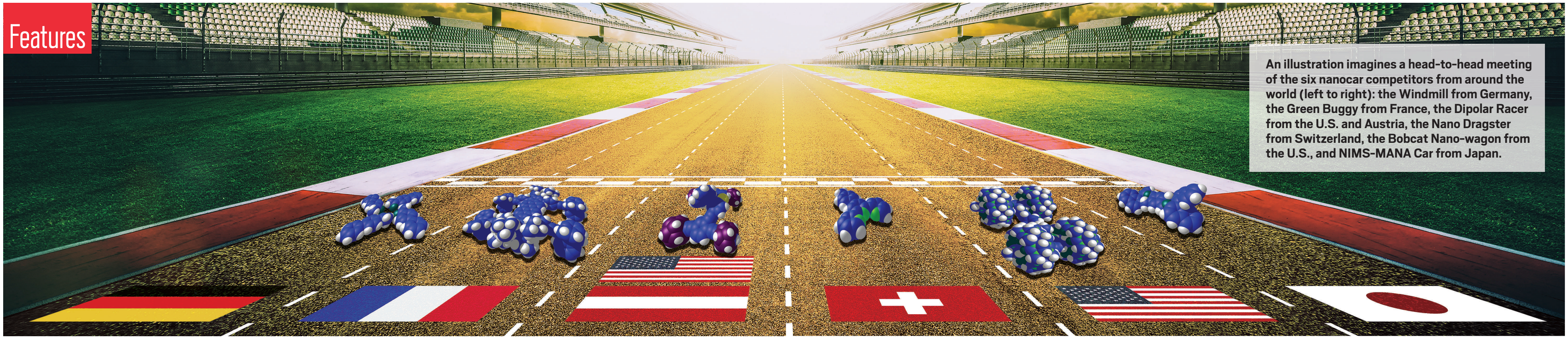

An illustration imagines a head-to-head meeting of the six nanocar competitors from around the world (left to right): the Windmill from Germany, the Green Buggy from France, the Dipolar Racer from the U.S. and Austria, the Nano Dragster from Switzerland, the Bobcat Nano-wagon from the U.S., and NIMS-MANA Car from Japan.

MOLECULAR MACHINES

World's first nanocar race crowns champion

C&EN follows the action on and off the track

MATT DAVENPORT, C&EN WASHINGTON

It's hard to understand why Eric Masson's excited about a picture of his car with a missing wheel. The fact that the car in the sepia micrograph on his computer screen looks more like a toasted marshmallow than a Maserati doesn't help, either. But Masson, a supramolecular chemist at Ohio University, patiently explains that the lumpy, cream-colored rectangle he's pointing to in the scanning tunneling microscope (STM) image is an assembly of atoms that scientists can drive across a surface. It is a nanocar.

There are several similar rectangles in this STM image. All of them, except for one, feature four discernible lumps, one at each corner. These lumps are nanocar wheels made of large, ring-shaped cucurbituril molecules.

But the car Masson's pointing at has only three lumps. Resting nearby is a bright circle—a cucurbituril wheel lying on its side.

The car missing its wheel refuses to move, Masson has learned from his colleague and STM sage, Saw Wai Hla. Perplexingly, this is exciting news.

Masson, Hla, and their coworkers make up one of six international teams preparing for the first-ever nanocar race on April 28 in France. Because Ohio University is within driving distance of C&EN headquarters—using a macroscopic car, of course—we were able to visit the team.

So here we are, two weeks before the race, staring at the team's immobile three-wheeler. The naïve nanocar observer wonders what happens if this hobbled molecule takes to the track against more ambulatory competition. The thought generates feelings closer to anxiety than excitement.

But Masson has a different, more complete view of his nanocars and the race as a whole. From a simple standpoint, the race is a friendly international competition that will showcase new STM technology at the French National Center for Scientific Research (CNRS) in Toulouse.

But the bigger picture is that the race is giving molecular machinists a platform to show where the field is headed. And, for the researchers involved, synthesizing and racing the nanocars has presented rich opportunities to push the limits of new technology and learn new science, Masson says.

That helps explain why he's excited about the broken, motionless car. It raises a host of questions he and his team could choose to answer for the first time. For example, why isn't it moving? And for the four-wheeled cars that do move, do the wheels skid or roll along the surface? (The team has started looking into that question, and early evidence suggests rolling, Masson says.)

Even seeing the lost cucurbituril wheel lying on its side was exciting for the Ohio team. Nobody had ever imaged that with an STM before. Researchers are seeing and manipulating molecules on surfaces like never before, which could open new doors in surface chemistry and solid-state technology.

Masson's perspective is best captured in the three possible outcomes he sees for the race. The first is that the Ohio team wins. The second outcome is the team loses. The third is the team loses because its molecular car does something totally unexpected during the race. "That outcome is the most exciting one to me," Masson says.

There is, however, one more feature in the image on Masson's screen that suggests he'd also be happy with the first possibility. Between the lumpy rectangles are a handful of horizontal beige lines. The team thinks these are blurs in the image created by four-wheeled nanocars zipping by the STM probe as it "photographs" the surface. The molecular cars are literally streaking across the screen.

"Apparently these things fly," Masson says, smiling.

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On your ever-so-tiny mark

The rules of the race are fairly straightforward. Each team will drive its car along a 100-nm-long, S-shaped racetrack made from gold inside an STM. The teams will propel their vehicles using an STM tip, a narrow tungsten rod sharpened to an atomic point.

Mechanically pushing the cars with the tip is not allowed during the race, but teams can nudge their cars to the starting line. Once the race starts, each team will position an STM tip near its car and fuel the molecular vehicles with electrons and electrical energy, which drivers control by modulating the tip's voltage. The first team to complete the course wins.

The basic guidelines disguise the myriad complexities of coordinating a molecular-scale race, not to mention the multitude of opportunities for things to go wrong. "I feel like we're launching a rocket," says race organizer Christian Joachim, a researcher in the Nanosciences Group at CNRS. "We have to make sure all the little technical details are accounted for."

Along with his collaborator, Gwénaël Rapenne, Joachim first publicly proposed the idea of a nanocar competition back in 2013 (*ACS Nano*, DOI: 10.1021/nn3058246). After that, it took about three years to put together a budget, find sponsors, and select the six racing crews.

Rapenne is actually leading one of those teams, the Toulouse Nanomobile Club. The team synthesized a $C_{184}H_{116}$ nanocar dubbed the Green Buggy.

The Green Buggy will be one of four nanovehicles racing inside a state-of-the art, four-tip STM at CNRS. Although multitip STMs are not new, this one can achieve picometer resolution with each of its tips, and that is totally new, Joachim says. Beyond driving nanocars, this will help more intimately probe the electrical properties of molecules, he predicts.

The CNRS instrument will enable four separate teams to simultaneously move and manipulate molecules in a manner that's never been attempted before.

Remember, though, there are six teams. All of them will be present in Toulouse, but the Ohio team and a team of Austrians and Americans will remotely control their cars. Thus, only four nanocars will physically be in Toulouse.

The remaining two will be controlled by pilots in Toulouse linking up to their own STMs in Ohio and Austria, Ohio's Hla says.

That means Ohio's drivers will be moving an STM tip and their car with nanoscopic precision from across an ocean. If that impresses Hla, it doesn't show. "That's today's technology," he says, matter-of-factly.

Still, all this technology has steered the nanocar race into uncharted territory, and as anyone who has played Oregon Trail can attest, pioneering is fraught with broken wheels and axles.

"Anything can happen," says James M. Tour, a leader of the American-Austrian Nanoprix Team and a synthetic organic chemist at Rice University. Tour also led the first team to unveil a single-molecule car, as C&EN reported back in 2005 (Oct. 24, page 13).

Cars could get stuck in single-atom imperfections along the gold-paved track, he explains. Or STM tips could crash into the surface. Or maybe a car just isn't optimized for the STM driving it. There are a lot of unknowns, he says.

Still, he's happy to see the excitement and interest around nanomachinery. Tour has been working on nanocars for nearly 20 years and the work was slow going early on, but that's changing. "Molecular-scale control, on a surface, is now taking off in a big way," he says.

Sander Otte of the Delft University of Technology is a master at manipulating atoms with STMs. Although he's not part of the race, he is a fan. "It is fantastic that events like these are being organized," he comments.

But he also thinks it may be a little generous to label all of the race's entrants as true nanocars, especially compared with the work of newly minted Nobel Laureate Ben L. Feringa.

Feringa and his team developed molecular machines with moving parts energized by light or electric current, for example. The motion of these parts translates to motion of the entire molecule, like a car carried by its rotating wheels powered by the vehicle's engine. Molecular machining has allowed nanocars to shift from neutral to drive.

Based on the information available to C&EN on the race's website, the Green Buggy may come the closest to that advanced standard. Other cars in the race are more like

"Having an element of competition always inspires people to come up with creative solutions and try out new ideas."

Sander Otte, Delft University of Technology passive wagons that can be towed around the surface using an STM tip's electric field.

"Still, we shouldn't be too critical," Otte concludes, adding that he hopes there are more nanoraces in the future. "Having an element of competition always inspires people to come up with creative solutions and try out new ideas."

Feringa politely declined to comment on this story, as did fellow molecular machinists and 2016 chemistry Nobel Laureates J. Fraser Stoddart and Jean-Pierre Sauvage.

Get synthetically set

The defining feature of the Ohio team's Bobcat Nano-wagon is its wheels. Focusing on these, however, rolls over a complicated synthesis executed by grad students Mersad Raeisi, Kondalarao Kotturi, Ramin Rabbani, and postdoc Karthikeyan Perumal.

The crew perfected a process that linked a terphenyl drive shaft with axles made from 4-phenylpyridine groups using benzimidazolium motifs, Raeisi explains. This frame is comparable in size to other cars in the contest, but adding the cucurbituril wheels makes it the most massive of the racing molecules.

It's about four times heavier than the next closest competitor, Masson says, although weight doesn't matter much at this scale. Still, that doesn't stop the team from affectionately joking about their molecule.

"It's like a monster truck," Kotturi says. "It's a real American car," Rabbani adds.

The French and Austrian-American teams have also created molecules that resemble familiar car shapes with wheels and axles, though they're more compact. Led by Rice's Tour and Leonhard Grill of the University of Graz, the latter team enters the competition with a Racer X mystique, having kept the precise design of their molecular car, the Dipolar Racer, a secret.

The remaining three molecules look like things that are decidedly not automobiles.

The Swiss Team considers its Nano Dragster more of a hovercraft than a car. Led by Rémy Pawlak and Ernst Meyer of the University of Basel, the team's flat, triangular $C_{22}H_{17}N_3$ molecule is designed to glide across the gold surface.

The German Nano-windmill Company also opted for a flat nanocar. As the team's name suggests, the molecule resembles a windmill's wheel made up of four acetylbiphenyl blades.

The outer edge of each blade provides a steering point to control the molecule with an STM tip. The team, led by Francesca Moresco of Dresden University of Technology, believes its design will provide an advantage in handling the race's two turns.

The Japanese team's nanovehicle is perhaps the most unique. The group will pilot a binaphthyl dimer designed by team leader Waka Nakanishi of the International Center for Materials Nanoarchitectonics, a Japanese research institute.

The dimer has two naphthyl "paddles" connected to a short organic chassis. One paddle's in the front and the other is in the back. The paddles should swing in and out when excited by the STM tip, allowing the molecule to scoot along the racetrack like an inch worm, Nakanishi explains.

She was initially unsure this approach would work, but the organic chemist was excited by the prospect of exploring the molecules she works with in a new way.

"Our molecules are soft and flexible," she says. "STM people don't tend to look at them." Teaming up with STM scientists to take on the challenge of imaging and driving the molecule has been one of the most rewarding experiences of the race, she says.

She's speaking scientifically, but there is a fiscal component to that sentiment as well: A massive automotive company is sponsoring the team and its nanoscopic car.

"Toyota shares our spirit, the spirit to challenge ourselves and our technology," Nakanishi says.

And Toyota isn't the only car company supporting the nanoaction. Volkswagen and the French automaker PSA Groupe are sponsoring the German and French competitors, respectively.

Go, little nanocars, go

Back on the Ohio University campus, hanging outside Masson's lab is a poster about the Bobcat Nano-wagon, complete with the molecule's nuclear magnetic resonance signature. It conjures up an idea for a bumper sticker: My other car has an NMR spectrum.

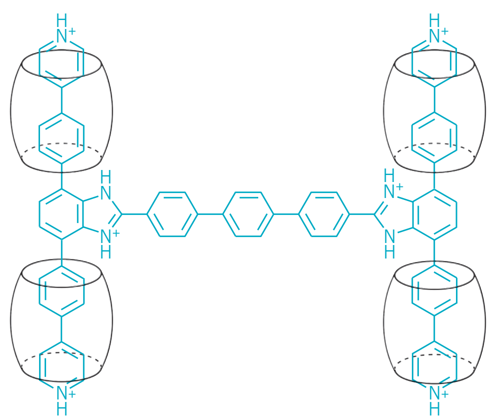
"Chemists can see that NMR spectrum and know they've got what they want, but we physicists need to see it," says Hla, Ohio's STM expert. And this brings us back to that image of the car missing the wheel.

Hla made that image by taking a solid nanocar powder, pumping it down to a vacuum inside the STM chamber, and then sublimating individual cars onto a surface at roughly 5 K. This is the same procedure each team will use to deposit its car onto the official racetrack.

Hla's plan for the race is to line up several cars near the starting line. Being able to prep like this ensures the team can pick only four-wheeled cars, meaning that they don't have to worry about the broken-down three-wheeled variety.

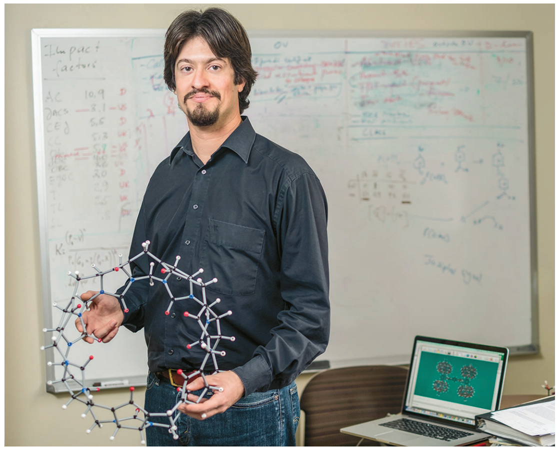
Having a "parking lot" near the starting line serves another purpose for the zippy Bobcat Nano-wagon. There's a chance Hla or the team's other driver, undergraduate student Ryan Tumbleson, could lose control of the speedy molecule during the race. If a car goes careening off the track, the driver can move the STM tip back to the starting line and start over with one of the waiting cars.

But speedy in this race is best measured in fractions of nanometers per minute. This, combined



Masson holds a 3-D printed model of the Ohio Bobcat wagon, with its chassis structure shown. The large circular shapes represent the cucurbituril wheels.

CREDIT: MATT DAVENPORT/C&EN



Masson (left) holds a model of a cucurbituril molecule, with the Ohio University nanocar visible on the laptop behind him. Hla (right) peers into an STM chamber.

CREDIT: ROB HARDIN/OHIO UNIVERSITY

with the potential for any number of nanocar accidents, is why the teams have a maximum of nearly 40 hours to complete the race.

Hla's not sure if the race will take that long, but he seems more focused on a much longer timescale anyhow.

To him, the race is about changing the way people think about chemistry. It's moving from moles of reactants in a solution to single molecules on a surface. This level of control could open up new doors in electronics, communications, and synthesis.

He cautions against overhyping these applications and says they are still far, far away, but he hopes the race will get more people thinking about the possibilities.

In the nearer term, the race is already capturing the public's imagination. Hla had to postpone an interview with C&EN to make time for a French TV news crew. Masson and team says their participation has helped them more easily communicate their work with friends and family.

It's cliché, but this seems like a race where everyone has already won. But, of course, everyone still wants to win.

The victory lap

We learned on the day of the race that Hla's uncertainty was warranted. Although the race was officially called after 30 hours, the Dipolar Racer sped across the finish line in just about 90 minutes, earning a first place finish for the team led by Tour and Grill.

This nanocar—a two-wheeler with tires made of adamantine—was so fast that the researchers had handicapped themselves by adding 50 nm to their racetrack in Austria. They also raced on silver instead of gold to further slow the car. Tour and Grill plan to publish the full design of the car, according to a press release from Rice.

About five hours later, the hovercraft-like Swiss Nano Dragster became the only car to complete the race on a gold track. CNRS declared the Swiss team a co-winner of the race, along with the U.S.-Austria team.

The Bobcat Nano-wagon got stuck 43 nm into the race, but it covered the most distance of the teams not to finish, putting the Ohio team in third place.

"Our nanocar was able to move as expected, and we learned quite a lot," Hla says, adding that his team made history by racing a nanocar from across an ocean. This was made possible by grad students Kyaw Zin Latt and Sanjoy Sarkar, who maintained the STM in Ohio.

And the team earned another distinction in Toulouse, Hla continues. "We got the 'Texan prize' for operating the largest-ever functional nanocar." ■